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PREPARATION AND CHARACTERIZATION OF COPPER(II) OXIDE SINGLE CRYSTALS
BY CHEMICAL VAPOR TRANSPORT

by

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PREPARATION AND CHARACTERIZATION OF COPPER(II) OXIDE
SINGLE CRYSTALS BY CHEMICAL VAPOR TRANSPORT

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ABSTRACT

Single crystals of copper(II) oxide were grown by chemical vapor transport using tellurium(IV) chloride and hydrogen chloride as transport agents. Hydrogen chloride provided better transport resulting in larger crystals. The crystals were characterized by x-ray diffraction, magnetic susceptibility and electrical resistivity. Crystals grown using TeCl_4 as a transport agent were p-type semiconductors with $\rho = 1300 \Omega\text{-cm}$ at 25°C and an activation energy of 0.11 eV. Crystals grown using HCl had $\rho > 10^6 \Omega\text{-cm}$.
MATERIALS INDEX: Copper oxide, Single crystal growth

Introduction

Copper(II) oxide occurs as the mineral tenorite and crystallizes with a monoclinic unit cell with the C2/c space group. In copper(II) oxide, the Jahn-Teller distortion due to the stabilization of a single d-hole per atom, Cu(II)3d^9 , results in the observed difference of its structure with the monoxides of the first row transition metals. This unique structure also gives rise to unusual magnetic and electrical properties.

Single crystals of CuO have been prepared by flux growth (1), sublimation (2) and chemical vapor transport (3,4). These investigations were primarily concerned with the preparative crystal growth where characterization was limited to x-ray diffraction and in some cases to magnetic susceptibility. Electrical studies were not performed. In this study, single crystals of copper(II) oxide were prepared by chemical vapor transport using tellurium(IV) chloride and hydrogen chloride as transport agents. Gray et al. (5) demonstrated that TeCl_4 oxidized crystals of V_2O_3 as opposed to HCl, which was shown to be a non-oxidizing transport agent. The V_2O_3 crystals grown using TeCl_4 as a transport agent were shown to contain V_3O_5 . Since TeCl_4 is an oxidizing transport agent whereas HCl is not, an investigation of the effect of preparation on the electronic properties of CuO was undertaken. The use of TeCl_4 as a transport agent should increase the amount of Cu(III) present as opposed to crystals grown in the presence of HCl.

Experimental

Preparation

Single crystals of CuO were grown by chemical vapor transport using hydrogen chloride and tellurium(IV) chloride as transport agents (100 torr of hydrogen chloride and a concentration of 2.3 mg/cm³ tellurium(IV) chloride were used). Polycrystalline CuO used as the starting material was prepared by oxidizing copper metal (Johnson Matthey, 5-9's) in air. The copper metal was heated in air at 600°C for 24 hrs in a porcelain crucible. The resulting powder was ground and reheated in air at 600°C for 24 hrs. Charge-growth gradients of 890-830°C were used for crystals grown using HCl and gradients of 810-750°C were used for TeCl₄ grown crystals. Crystal growth was allowed to proceed for 12 days in both cases. Crystals grown were primarily plate-like with dimensions up to 5 x 3 x 0.2 mm³ for HCl grown crystals and 2 x 2 x 0.2 mm³ for crystals grown with TeCl₄ used as a transport agent.

X-ray diffraction analysis

Single crystals were finely ground between glass plates, and a thin layer of the resulting powder was dispersed with acetone on a glass slide. Powder diffraction patterns were obtained with a Philips-Norelco diffractometer using monochromatic high intensity CuK α_1 radiation ($\lambda = 1.5405\text{\AA}$). For qualitative identification of the phases present, the patterns were taken from $12^\circ < 2\theta < 72^\circ$ with a scan rate of $1^\circ 2\theta/\text{min}$ and a chart speed of 30 in/hr. Cell parameters were determined by a least squares refinement of the reflections using a computer program which corrects for the systematic errors of the measurement.

Annealing experiments in oxygen

Crystals were placed on a silica boat and loaded into a horizontal furnace. The oxygen passed through a P₂O₅ drying tube and was allowed to purge for 2 hrs. The temperature was increased to 650°C at a rate of 75°C/hr, held at 650°C for 10 hrs and cooled at a rate of 75°C/hr to room temperature.

Magnetic measurements

Magnetic susceptibility measurements were carried out using a Faraday balance from 77 to 300 K with a field strength of 10.4 kOe. Honda-Owens (field dependent) measurements were carried out at 77 and 300 K.

Electronic measurements

The resistivities of single crystals were measured from 200 to 330 K using the van der Pauw (5) technique. Contacts were made by ultrasonically soldering indium metal to the edge of the crystal. Ohmic behavior was established by measuring the current-voltage characteristics. A qualitative Seebeck voltage measurement was made to determine carrier type.

Results and Discussion

Single crystals were grown in this study by chemical vapor transport using tellurium(IV) chloride and hydrogen chloride as transport agents. The crystals grown were shiny black platelets. Larger crystals were obtained using hydrogen chloride as the transport agent, with the largest crystals growing as



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twinned aggregates. Although previous investigators have prepared CuO crystals by various techniques, the effect of crystal preparation on the electronic properties was not undertaken. This study examines the effect on the electronic properties of CuO crystals prepared with oxidizing and non-oxidizing transport agents, with the oxidizing transport agent favoring the presence of Cu(III).

The crystal structure of copper(II) oxide (7) shows Cu(II) with square planar coordination of oxygen around the copper. The space group is C2/c with unit cell dimensions of $a = 4.6837(5)\text{\AA}$, $b = 3.4226(5)\text{\AA}$, $c = 5.1288(6)\text{\AA}$, and $\beta = 99.54^\circ(1)$. Fig. 1 shows the chains of square planar copper-oxygen bonds. The chains traverse the structure in the [110] and $[-110]$ directions and each type of chain is separated by 2.7Å. The structure is a distorted PdO type, and each copper has four O' neighbors at 1.96Å and two next nearest O'' neighbors at 2.78Å. Cell parameters obtained for copper(II) oxide single crystals are shown in Table I. It can be seen that there is no difference in the cell parameters of the CuO crystals obtained using TeCl_4 or HCl as transport agent.

Table I
X-ray and Preparative Data for CuO

Process	Charge-Growth Gradient ($^\circ\text{C}$)	Cell Parameters			
		a(Å)	b(Å)	c(Å)	$\beta(^\circ)$
CVT(TeCl_4)	810-750	4.684(2)	3.422(2)	5.123(2)	99.60(1)
CVT (HCl)	890-830	4.683(2)	3.420(2)	5.122(2)	99.60(1)

O'Keefe and Stone (8), as well as Roden (9), have indicated that CuO is antiferromagnetic with an observed anomaly in the magnetic susceptibility at 230 K. Recent neutron diffraction studies by Yang et al. (10) and Forsyth et al. (11) have confirmed antiferromagnetic behavior in CuO with a Néel temperature of 230 K. In this study, magnetic susceptibility measurements confirmed the Néel point and atypical behavior of CuO.

Crystals suitable for electronic measurements were approximately $2 \times 1 \times 0.2 \text{ mm}^3$. Crystals grown by CVT using TeCl_4 as a transport agent were p-type semiconductors with resistivities of $1300 \Omega\text{-cm}$ at 25°C . A plot of $\log \rho$ vs $1000/T$ for a typical crystal grown by CVT using TeCl_4 is shown in Fig. 2. For temperatures below 200 K the resistance of the samples was too high and did not give reliable data. The activation energy was determined to be 0.11(1) eV in the temperature range shown in Fig. 2.

Electronic measurements on single crystals grown by CVT using hydrogen chloride as a transport agent were made on several crystals; all showed higher resistances than $10^6 \Omega$, corresponding to $\rho > 10^6 \Omega\text{-cm}$ at 25°C with carrier type undeterminable. Crystals of CuO grown using HCl were annealed in flowing oxygen at 650°C . These crystals became p-type with $\rho = 2 \times 10^5 \Omega\text{-cm}$. Current work (12) on polycrystalline CuO has shown that it can contain small amounts of Cu(III) resulting in semiconducting behavior; and the amounts of Cu(III) can be altered only slightly under various annealing conditions. The lower resistivity of the CuO crystals grown in TeCl_4 may be caused by a slight

Fig. 1. Structure of CuO.

Fig. 2. Resistivity as a function of temperature for a crystal of CuO grown with TeCl_4 as transport agent.

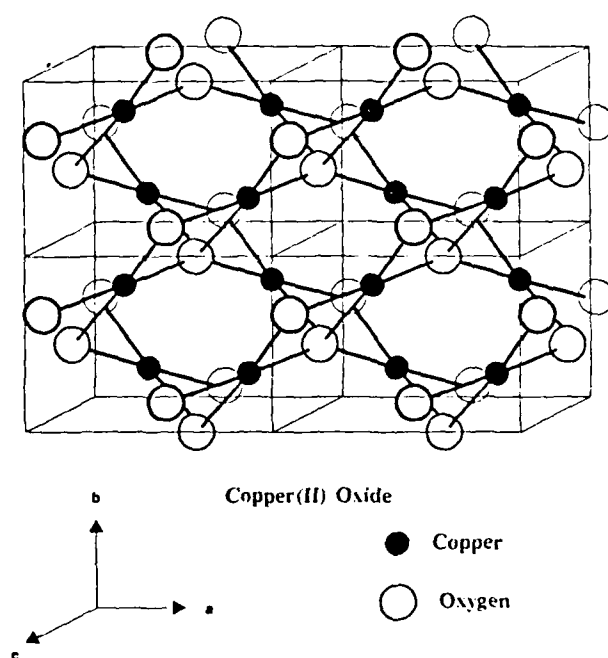


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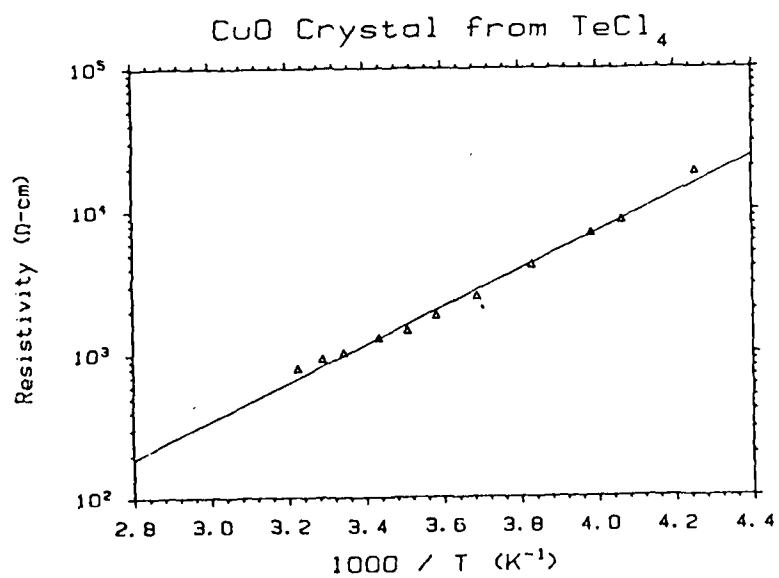


Fig. 2. Resistivity as a function of temperature for a crystal of CuO grown with TeCl_4 as transport agent.

increase in Cu(III) as a result of the oxidizing nature of the transport agent. Crystals grown in HCl showed a high resistivity indicating a more stoichiometric material. The resistivity of the HCl grown crystals was lowered by annealing in oxygen to $2 \times 10^5 \Omega\text{-cm}$ which is consistent with the introduction of small amounts of Cu(III).

Conclusion

Single crystals of copper(II) oxide were prepared by chemical vapor transport using tellurium(IV) chloride and hydrogen chloride as transport agents. X-ray diffraction showed the crystals to be single phase copper(II) oxide crystallizing with a monoclinic unit cell of space group C2/c. Magnetic susceptibility indicated an antiferromagnetic anomaly at 230 K consistent with the magnetic behavior reported for copper(II) oxide. Crystals grown using TeCl_4 as a transport agent gave p-type semiconductors with $\rho = 1300 \Omega\text{-cm}$ at 25°C . High resistivity crystals grown with HCl were annealed in oxygen resulting in a lowering of the resistivity to $2 \times 10^5 \Omega\text{-cm}$ at 25°C . The difference in resistivity of samples prepared using TeCl_4 and HCl as transport agents could be a result of the introduction of small amounts of Cu(III) into crystals grown using TeCl_4 because of its oxidizing nature. The lowering of the resistivity of the annealed sample is also consistent with the introduction of small amounts of Cu(III). The presence of the Cu(III) content could only be determined through electrical resistivity measurements.

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